LA-UR-18-29657
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Author(s): Kim, Seung Jun
Naranjo, Mario Reyes
Wilkerson, Robert Blake

Intended for: Report

Issued: 2018-10-11

The ARGUS Solution Reactor and Molybdenum Production:

A Summary Report Based on Open Literature

Mario R. Naranjo, R. Blake Wilkerson, Seung Jun Kim

Nuclear Engineering and Nonproliferation

LOS ALAMOS NATIONAL LABORATORY (LANL)

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1 Summary

The (Aqueous Homogeneous Reactor) AHR was conceptualized at Los Alamos for work in advancing weapon design with initial experiments completed at Los Alamos National Laboratory (LANL) and Oak Ridge National Laboratory (ORNL) in the early 1940s and 1950s. The reactor design was discovered to be an efficient mean of production for medical radioisotopes (e.g. molybdenum-99 and other fission products) due to its streamlined process of extracting target radioactive sources from the fissile solution via a separation system. As the demand for medical radioisotopes has increased so has the need for a safe and low cost isotope source, the most commonly used of which is technetium-99m (^{99m}Tc), daughter product from molybdenum decay. Studies indicate solution reactors pose a significantly lower hazard to the workers, public and environment, compared to other modern reactors (International Atomic Energy Agency 2008). The inherent safety and ability to selectively extract radionuclides from its fuel solution make AHRs particularly well suited for medical isotope production. This discussion narrows its focus to one of the longest running aqueous homogeneous reactor systems, ARGUS. A study of the conversion of ARGUS to a low-enriched uranyl (LEU) sulfate fuel solution was part of the Global Threat Reduction Initiative (GTRI) program. The goal of this paper is to provide a summary of the ARGUS reactor system based on open literature available.

2 Background

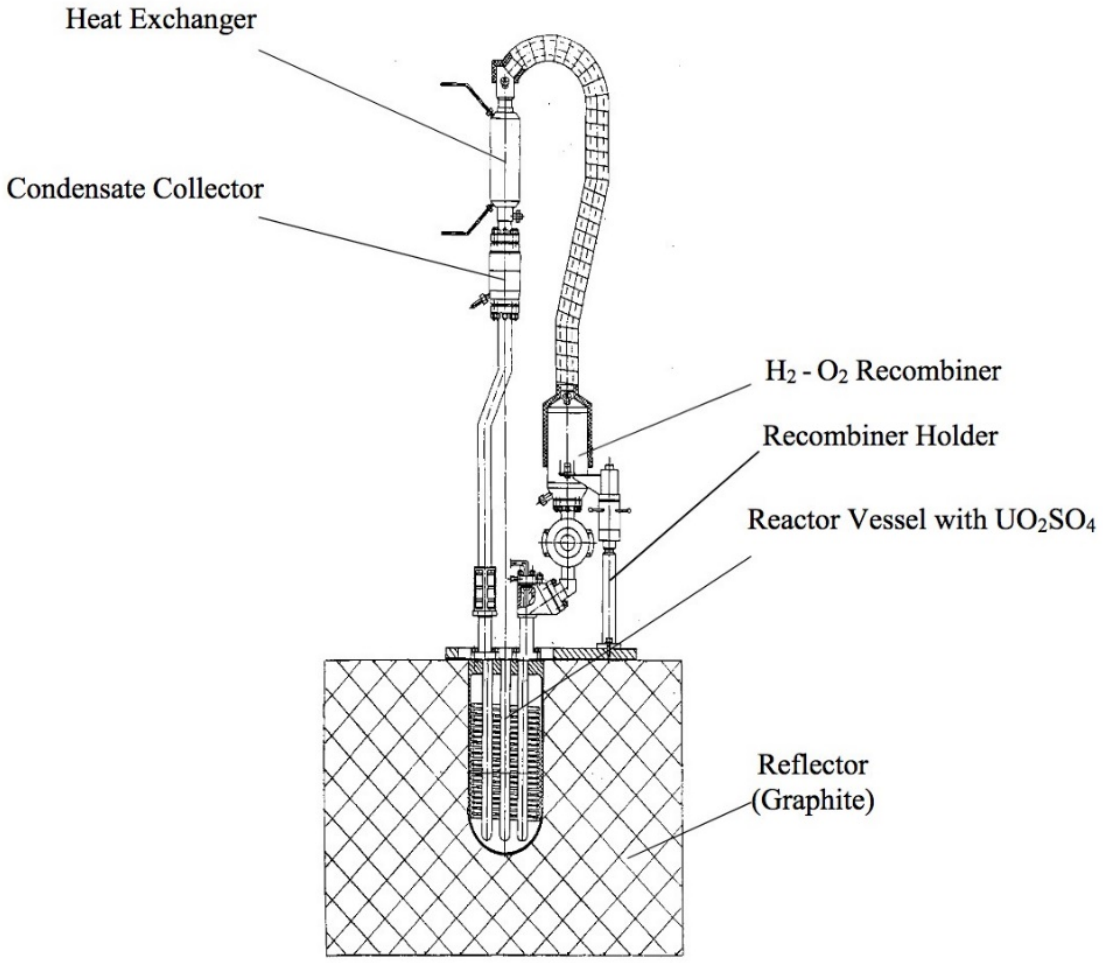


Figure 1: ARGUS Reactor design configuration depiction (P.L. Garner October 12-16, 2014)

The ARGUS AHR has been in operation since 1981 at the National Research Centre "Kurchatov Institute", the basic design configuration of which is illustrated above in Figure 1. For over 30 years this reactor has operated with a capacity of $50\ kW^{th}$ (R.W. Brown 2005), commonly run at $20\ kW^{th}$, using a highly-enriched uranyl (HEU) sulfate fuel solution. In July of 2014, first criticality was reached following the reactor's conversion to a LEU fuel solution. The purpose of the ARGUS reactor has been, and remains, "to search for the best physical-technical solutions when developing nuclear-physical methods of analysis and control as well as to develop work on production of radionuclides" (P.L. Garner October 12-16, 2014). Increased usage and demand for medical isotopes has resulted in a greater interest from large state entities to produce these isotopes quickly and efficiently, e.g. AHR technology similar to ARGUS.

2.1 Critical Assembly System

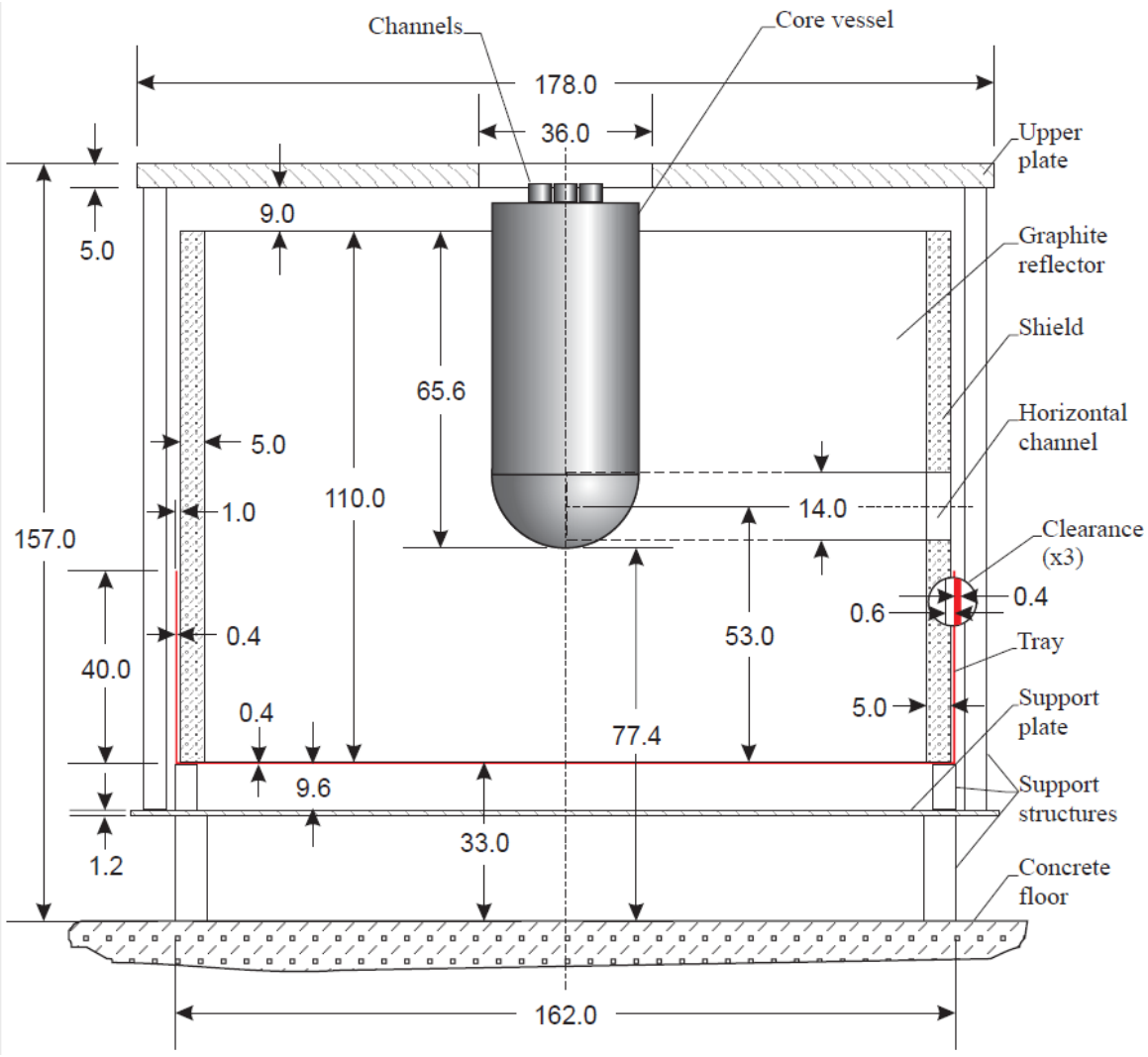


Figure 2: Critical Assembly Cross Section (dimensions given in cm) (Evgueni S. Glouchkov 1997)

The ARGUS reactor presently houses its low-enriched uranyl sulfate solution in a welded cylindrical vessel with a hemispherical bottom and a lid, filled to a critical state. Core neutron economy is maintained by surrounding the stainless steel vessel with a graphite reflector that is horizontally encompassed by a borated polyethylene shield (Evgueni S. Glouchkov 1997), reference cross sectional view of critical assembly in Figure 2. In addition to serving as a neutron reflector, the graphite provides a means for passive heat transfer from the system before being dissipated into the environment (Yu.D. Baranaev 2007).

Note: Figures 2 through 4 are of ARGUS' HEU configuration and certain dimensions have changed since the LEU conversion, 2012-2014, to allow for the larger solution volume, etc.

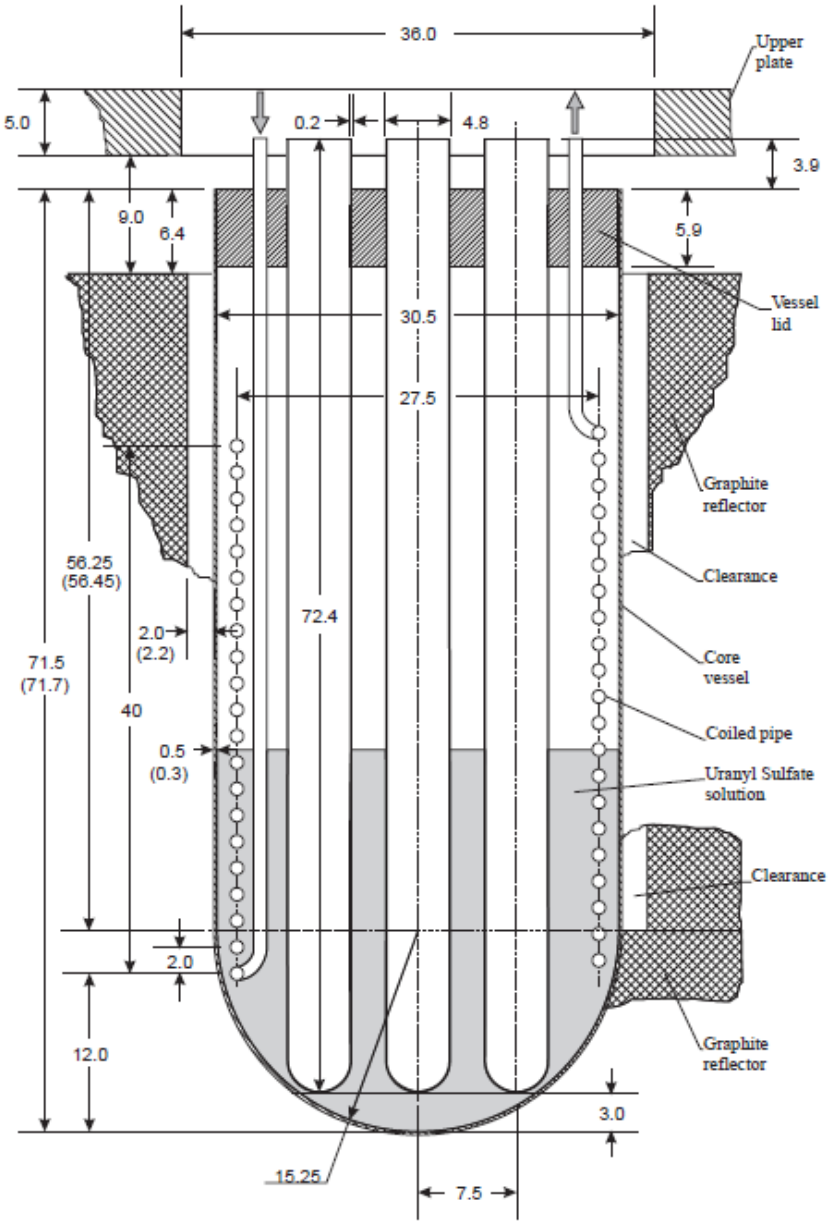


Figure 3: Longitudinal Section of the Assembly Core with Upper Plate and Vessel of 0.5 cm Wall Thickness, Dimensions for the Wall Thickness of 0.3 cm Given in Brackets (Evgueni S. Glouchkov 1997).

The inner vessel contains 3 stainless vertical dry channels, or zones, that pass through the vessel's lid, to the same depth in the fuel, for reactivity control. These zones are left empty, as gap zones, for use when control rods are needed. Control rods are used in the symmetric peripheral channels while an experimental target tube is placed in the center zone. Concentric to the vessel, is a stainless steel single helix cylindrical coiled cooling pipe containing distilled water (reference Figure 3). The graphite reflector is comprised of 25x25x50 cm machined blocks with a maximum fit gap of 0.1 cm (Evgueni S. Glouchkov 1997).

There are five circular vertical channels and one rectangular horizontal channel for neutron

beam rejection (Evgueni S. Glouchkov 1997) machined into the reflector, as illustrated in Figure 4. The five "dry" vertical channels are unlined and air filled, of which channel #4 extends through the entire height of the reflector, are used for performing activation analysis of materials (Pivovarov 2010).

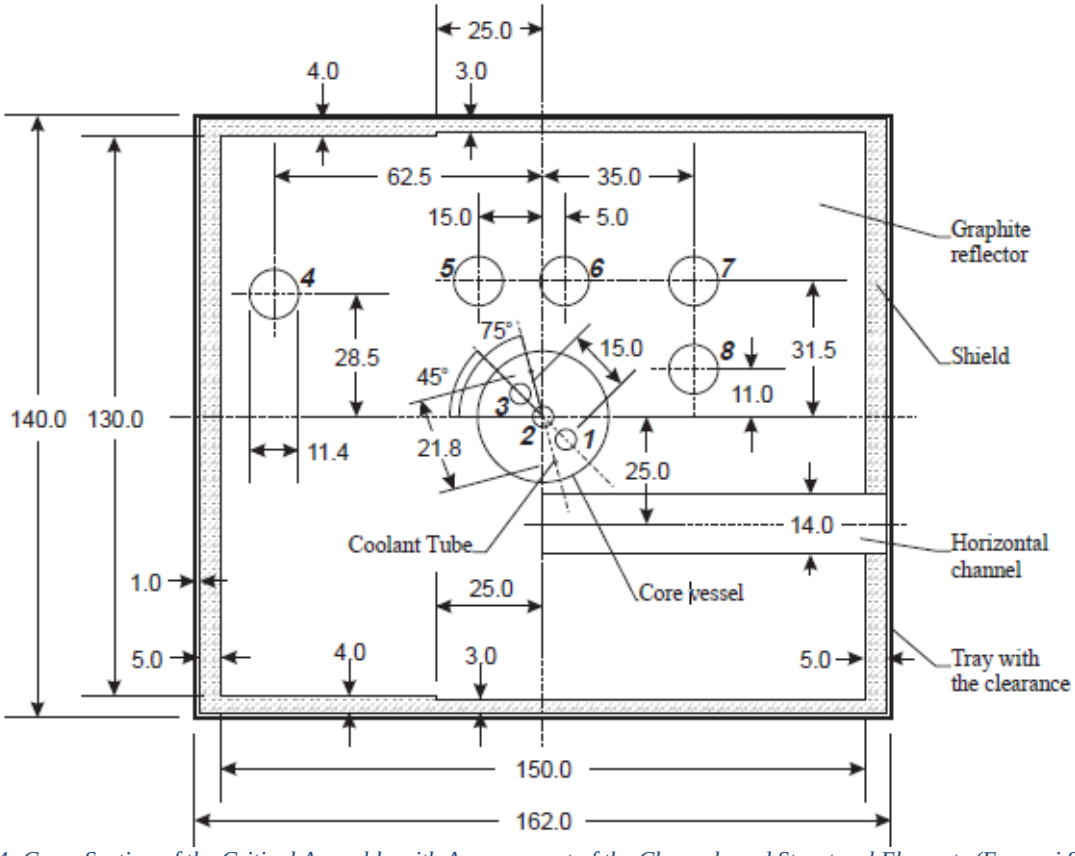


Figure 4: Cross Section of the Critical Assembly with Arrangement of the Channels and Structural Elements (Evgueni S. Glouchkov 1997)

A stainless steel tray surrounds the shield on five sides, fastened at its base to a ST-3 steel lower support plate. Along with the base plate there is an upper plate built from the same material, these comprise the only steel elements that are not stainless.

2.2 Catalytic Regeneration System

The Catalytic Regeneration System (CRS) is a closed loop of the vessel driven by natural circulation, whence the inert radioactive gases are processed. This system contains a heat exchanger, condensate accumulator, recombiner assembly and necessary piping. The radiolytic process disassociates the water in the fuel solution into H_2O_2, H_2 and O_2 requiring the use of a recombiner assembly in the first stage to ensure a limited hydrogen concentration and produce steam. After the recombined water vapor passes through the heat exchanger, the aqueous condensate is gathered at the accumulator, a portion of which is used for water flush of the sorption column (International Atomic Energy Agency 2008), before being reintroduced to the fuel solution (reference Figures 1 & 5).

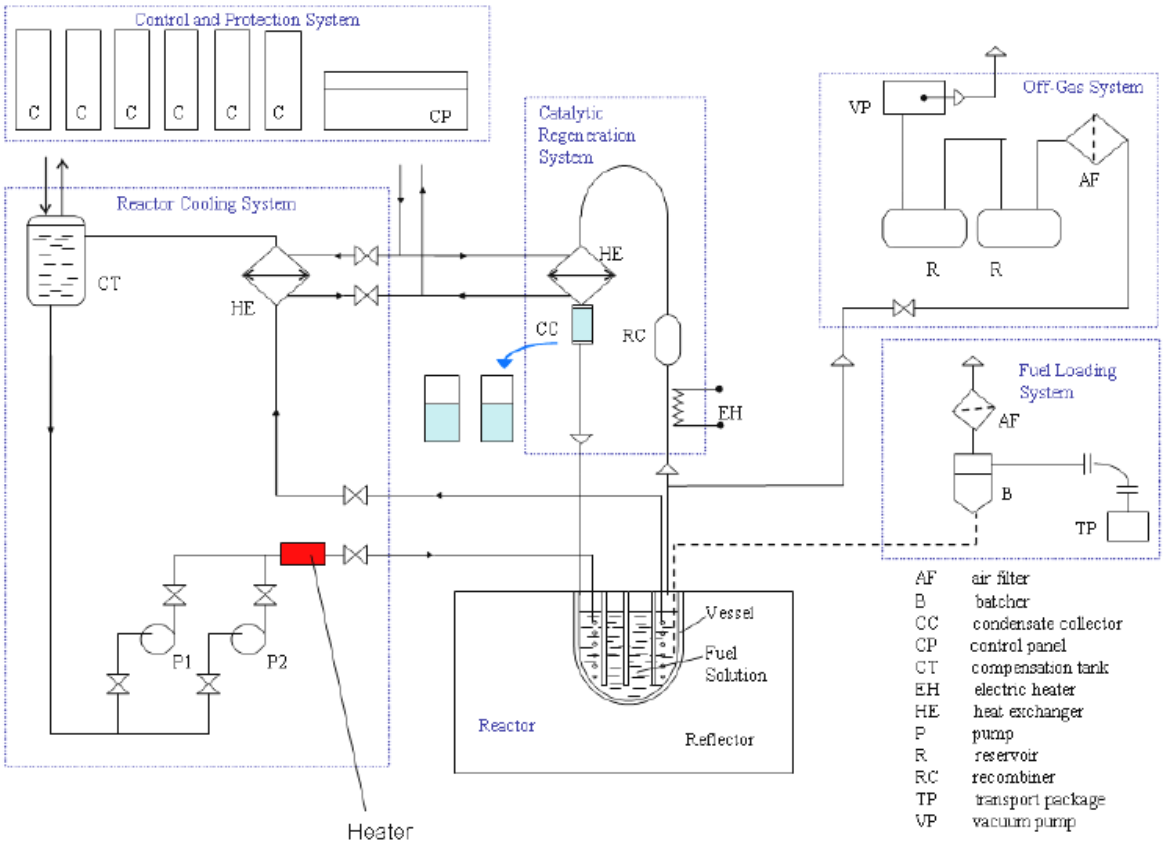


Figure 5: ARGUS Schematic Diagram (P.L. Garner October 12-16, 2014)

2.3 Cooling System and Inherent Safety Features

The ARGUS cooling system consists of two loops, which are pump driven. The primary cooling loop serves as a heat exchanger for the fuel solution in the vessel, coiled around the control tubes. The secondary cooling loop consists of two heat exchangers in parallel, one for the primary loop and the other for the CRS. Coolant in the vessel's coiled pipe flows from the lower to the upper portion of the coil via supply/return pipes of matching diameter and thickness (Evgueni S. Glouchkov 1997). The inherent safety features of ARGUS (1) passively maintain a low solution temperature, below boiling (90°C), by natural convection cooling, (2) self-regulate reactivity control by the negative reactivity feedback effect and (3) low reactor vessel pressure (less than atmospheric).

3 Thermal Hydraulics

There are two types of fuel solutions considered for aqueous reactors each utilizing uranium actinides solely:

- Uranyl Sulfate (UO_2SO_4)
- Uranyl Nitrate ($UO_2(NO_3)_2$)

The inert radioactive gases from the uranyl nitrate solutions include: hydrogen, oxygen, nitrogen and nitrogen oxide. The latter two have a detrimental impact on the AHR in terms of the system's stability and complexity. Whereas with uranyl sulfate solution, radiolytic bubbling only produces hydrogen and oxygen. With a simple recombiner loop, water is reintroduced to the fuel aiding in stability. Greater radiation stability is the primary reason uranyl sulfates are preferred over uranyl nitrates. From a processing yield perspective, irradiated uranyl nitrate solutions are preferred to irradiated uranyl sulfate solutions due to their higher distribution coefficient for ^{99}Mo extraction (see section 4.2 Recovery). "Because both salts have good and bad properties, a decision on which is superior requires additional experimental data and detailed system design. If the NO_x off-gas concerns are easily addressed, nitrate would be the salt of choice. If not, sulfate should be used" (International Atomic Energy Agency 2008).

3.1 Radiolysis

Radiolytic decomposition of the aqueous uranyl sulfate solution produces a significant amount of inert radioactive gases creating a bubble induced turbulence mixing effect. "The rate of gas production resulting from the radiolytic decomposition of water is a function of a number of parameters, including the acidity and uranium concentration of the fuel solution" (Remley, et al. 1958). This radiolytic bubbling plays an important role in solution reactor behavior, affecting not only power stability and thermal hydraulics, but neutronics as well. The process of radiolytic decomposition fluctuates the neutronics through the change of fissile solution density. In addition to temperature, radiolytic bubbles contribute to the fuel's volumetric expansion through void creation and dissipation of inert radioactive gases shown in Figure 6. Volumetric expansion results in a reduction of the solution density manifesting itself in a negative reactivity coefficient, reactivity control by the negative reactivity feedback effect. The amount of the radiolytic bubbles produced in the solution increases at higher power density, possibly resulting in significant reactivity variation due to reduced solution density and potential surface perturbation due to inert gas dissipation. Therefore, the power density, reactivity stability and solution composition play important roles in design and operation. While ARGUS power density is maximized at 1 kW^{th}/L of solution, tests are being considered to verify a power density of 2-2.5 kW^{th}/L is achievable for a future AHR system (International Atomic Energy Agency 2008).

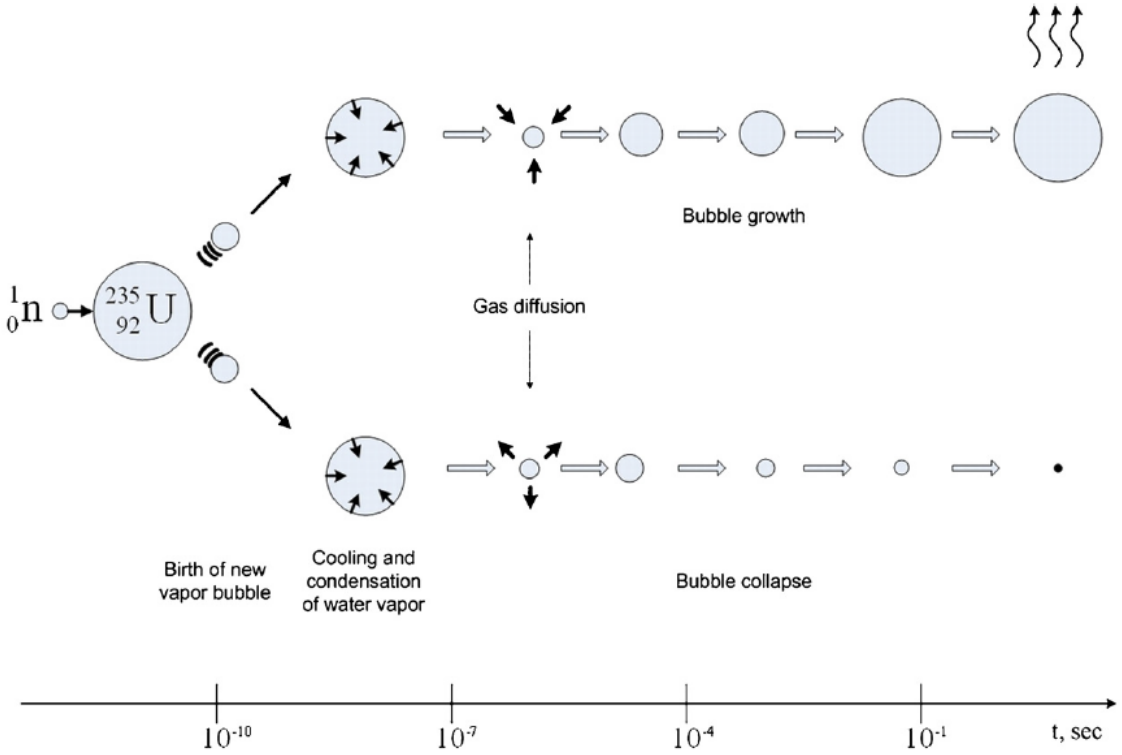


Figure 6: Scheme of Bubble Formation at Radiolytic Boiling (Chuvilin, et al. 2007)

3.2 Thermal Analysis

In the LEU converted ARGUS system, power is potentially restricted to 14 kW^{th} due to cooling limitations. This will produce significantly less ^{99}Mo since it is directly proportional to the power production. The LEU conversion has changed the density, heat capacity, radiolytic gas formation rate, solution height, etc. Each participates in the degradation of the cooling system's effectiveness. The increase in solution density and viscosity decreases "radiolytic boiling", resulting in a projected deterioration in solution mixing and homogenization during reactor operation. To counteract the new thermal-physical parameters, analysis advises a water chiller be introduced to the secondary cooling loop, thereby decreasing the primary loop's coolant temperature to 10 °C and possibly increase power by $2 - 4$ kW^{th} (S.V. Myasnikov October 14-17, 2012).

Based on a simulated experimental thermal analysis, achieving higher heat production (75 kW^{th}), will require more coolant coils or a different configuration to achieve the desired low temperature distribution in the fuel solution. To achieve higher heat production the addition of more coolant pipes or a different configuration is proposed (Daniel Milian Pérez 2015).

Note: 75 kW^{th} case study simulations result in temperatures greater than 90 °C, exceeding boiling temperature.

4 Neutronics and Recovery

4.1 Neutronics

The majority of medical isotope production reactors (MIPRs) irradiate targets in a neutron flux, typically generated by reactor fuel. In a solution reactor the reactor fuel is the target, where as in conventional target based reactors the ratio of reactor to target power is 100:1. Solution reactors produce an equivalent quantity of ^{99}Mo, while reducing the power consumption and generation of radioactive waste by a factor of approximately 100 (International Atomic Energy Agency 2008).

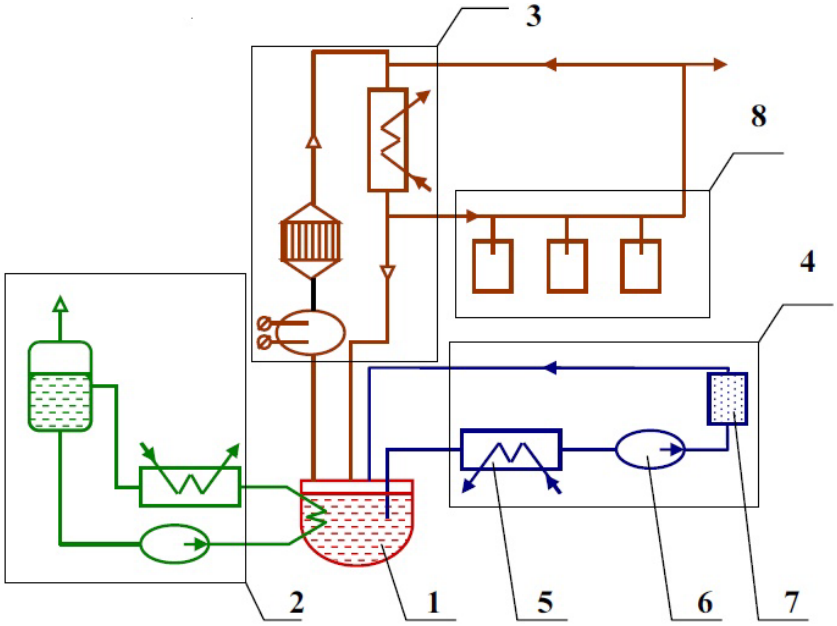
ARGUS utilizes a thermal neutron energy spectrum originally with enriched to 90wt% ^{235}U (i.e. HEU). After the conversion campaign, the enrichment was lowered to 19.8wt% ^{235}U (i.e. LEU). These adjustments increase the total uranium concentration significantly from 81.3 g/L to 380 g/L. The required operating volume of the fuel solution is also increased from 21.1 liters to 25.7 liters. Reactor characteristics were altered by increasing core height from 38 to 43 cm. This increased solution core height may diminish solution surface perturbation induced reactivity variations (International Atomic Energy Agency 2008). According to documents, the excess reactivity is 7.0 β_{eff} in the HEU original calculation and 4.0 β_{eff} in the LEU calculation. Experimental results from ARGUS with a HEU-fuel report a slightly lesser amount of excess reactivity at 6.3 β_{eff}. Peak thermal neutron flux of HEU is reported at 4.1e11 n/cm2-s and calculated at a lower value of 2.7e11 n/cm2-s for the LEU-fuel. Similarly, the fast neutron flux is reported at 0.8e11 n/cm2-s for HEU and 0.7e11 n/cm2-s and LEU configurations.

The increased quantity of ^{238}U in the LEU solution increases the production of ^{239}Pu, thereby increasing the absorption of neutrons. The increased ^{239}Pu alpha activity's effect on the ability of the ^{99}Mo extracted to meet United States Pharmacopeia (USP) requirements may necessitate modification of the purification process or addition purification steps (Russell M. Ball 1998).

4.2 Recovery

The ARGUS reactor utilizes a uranyl sulfate solution and in 2014 converted the system to a LEU solution. All off-gas treatment, water reintroduction, as well as solution addition and extraction is performed through the lid at the top of the reactor core (reference Figures 5 & 7). In terms of chemical extraction, the off-gas separation and recombination is simpler for uranyl sulfate than uranyl nitrate. Additionally, maintaining pH concentrations is critical for both sulfate and nitrate solutions. Nitrate fuel solution maintenance is more difficult due to the acidity of the NO_x gases, which are released causing the pH to rise. Therefore, the need of acid addition to the solution is significantly lower for uranyl sulfate reactor solutions (International Atomic Energy Agency 2008). However, the recovery of ^{99}Mo from a sulfate is not as efficient as a nitrate by anion exchange due to "more effective competition to sorption of $(MoO_4)^{2-}$ by the $(SO_4)^{2-}$ and $(HSO_4)^{2-}$ than by $(NO_3)^-$". Fundamental research has begun to use hydrated metal oxide sorbents to recover ^{99}Mo. Several types of sorbents including alumina, polyzirconium compound (PZC), and two types from Thermoxid (Isosorb & Radsorb) have

been studied. The significantly lower retention of ^{99}Mo by alumina compared to the Thermoxid and PZC sorbents indicates its inadequacy for use in the separation process.



Principal flow-sheet diagram of the Complex

1 – reactor; 2 – reactor cooling system; 3 – water regeneration system; 4 – Mo-99 recovery line; 5 – cooler; 6 – pump; 7 – Mo-99 extraction column; 8 – extraction line for the extraction of ^{89}Sr, ^{133}Xe, (^{131}I, ^{132}I, ^{133}I) isotopes from the fuel vapor-gaseous phase

Figure 7: Schematic from 2007 (Yu.D. Baranaev 2007)

An evaluation of ^{99}Mo separation from variable uranium concentrations in a sulfate solution at pH 1 using PZC, Isosorb and Radsorb (reference Figure 8). The Thermoxid sorbents have a higher partitioning or distribution coefficient (K_d in mL/g), the ratio of ^{99}Mo distribution in the uranyl sulfate solution, than the PZC. The Radsorb and Isosorb $K_d$values in a 350 g/L uranium concentration sulfate solution are 130 and 150, respectively. The previously stated uranium concentration following LEU conversion is 380 g/L, suggesting the Thermoxid sorbents are the most effective means of recovering ^{99}Mo.

The important effect on molybdenum redox chemistry by high radiation fields that will accompany fuel cooled for only a few hours is not fully characterized. Maintaining molybdenum in the (VI) oxidation state is essential to maximizing "its sorption in the loading phase and its stripping from the column in alkaline solution", since the molybdenum species of a lower oxidation state precipitate as hydrous metal oxides in the sorption column (International Atomic Energy Agency 2008). Studies report ^{99}Mo has a lower K_d value in a sulfate media four hours after irradiation. This information is obtained from limited resources and more research is necessary to account for this effect.

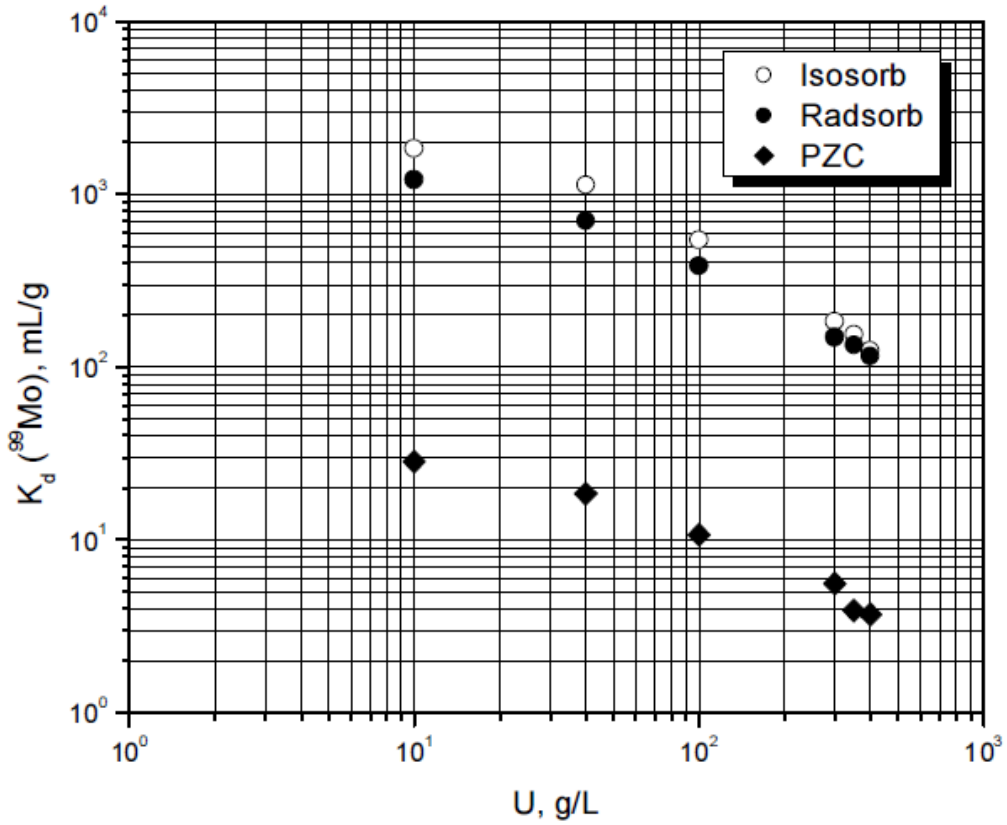


Figure 8: Effect of varying uranium concentrations on the uptake of trace levels of ^{99}Mo from H_2SO_4 solutions at pH 1 by the Thermoxid and PZC sorbents.

5 Conclusion

In conclusion, this study was conducted using the limited open literature resources available on the ARGUS reactor and its recent conversion to LEU. Despite current research and technology being well established, an increase in active contributions from state, commercial and pharmaceutical entities is required for further development of radioisotope technology. Key points from this summary report are as follows:

- From 2012-2014 ARGUS underwent a conversion from a highly enriched uranyl sulfate (i.e. 90wt% ^{235}U) to a low enriched uranyl sulfate (i.e. 19.8wt% ^{235}U) solution.
- Uranyl sulfate solutions was used in ARGUS reactors due to its greater reactivity stability and simpler off-gas recombiner process.
- Solution reactors produce an equivalent quantity of ^{99}Mo, while reducing the power consumption and generation of radioactive waste by a factor of approximately 100 compared to conventional target reactors.

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